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(54) ROOM TEMPERATURE CURING COMPOSITION AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition having sufficiently low viscosity, free from the loss of the flexibility of a cured material even in the case of using an inorganic filler and useful as a sealing material, etc., by mixing plural specific high molecular polymers having different molecular weights.

SOLUTION: (A) 100 pts.wt. of a high molecular weight polymer having a molecular weight of 8000-30000 in which $\geq 50\%$ total molecular terminal groups are hydrolyzable silicon-containing groups is compounded with (B) 1-200 pts.wt. a high molecular weight polymer of 4000-30000 in which $< 50\%$ total molecular terminal groups are hydrolyzable silicon-containing groups. Further, it is preferable that both the main chains of the component A and the component B are substantially polyethers and both the hydrolyzable silicon-containing groups of the component A and the component B be expressed by the formula R_2SiXaR^{13-a} [R¹ is a 1-20C (substituted) monovalent organic group; R² is a divalent organic group; X is OH or a hydrolyzable group; (a)=1-3]. Furthermore, preferably, (C) a plasticizer, especially free from a low molecular plasticizer, is contained or a plasticizer is not substantially contained.

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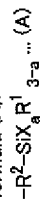
CLAIMS

[Claim(s)]

[Claim 1] Polymer (I) of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups. And a room-temperature-curing nature constituent in which less than 50% of all the molecular terminal groups contain one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups to polymer (I) 100 weight section.

[Claim 2] A room-temperature-curing nature constituent of Claim 1 whose both main chain of polymer (I) and main chain of polymer (II) are polyether intrinsically.

[Claim 3] polymer (I) --- a room-temperature-curing nature constituent of Claim 1 by which both a hydrolytic silicon group and a hydrolytic silicon group of polymer (II) are expressed with a following formula (A).



R^1 is a univalent organic group substitution of the carbon numbers 1-20, or unsubstituted among a formula, R^2 is a divalent organic group, X is a hydroxyl group or a hydrolytic basis, and a is an integer of 1-3.

[Claim 4] Claim 1, a room-temperature-curing nature constituent of 2 or 3 in which a room-temperature-curing nature constituent does not contain a plasticizer substantially.

[Claim 5] Claim 1, a room-temperature-curing nature constituent of 2 or 3 which a room-temperature-curing nature constituent contains a plasticizer further, and do not contain a low molecule plasticizer as the plasticizer.

[Claim 6] As opposed to polymer (I) 100 weight section of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups, A manufacturing method of a room-temperature-curing nature constituent, wherein less than 50% of all the molecular terminal groups mix one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the room-temperature-curing nature constituent hardened under hygroscopic-surface-moisture existence.

[0002]

[Description of the Prior Art] The method of making harden various kinds of polymers which have a hydrolytic silicon group, and using it for a sealing material, adhesives, etc. is known well, and is a useful method industrially.

[0003] The polymer especially whose main chain is polyether among such compounds is liquefied at a room temperature, and when a hardened material holds pliability also at low temperature comparatively and uses for a sealing material, adhesives, etc., it is provided with the desirable characteristic.

[0004] As a polymer of such hygroscopic-surface-moisture hardenability, the polymer of the hygroscopic-surface-moisture hardenability which has a hydrolytic silicon group is mentioned to the end indicated to JP.3-72527.A, JP.3-47825.A, etc. In the polymer which has a hydrolytic silicon group at such the end, although the pliability of a hardened material increases, the viscosity of a polymer becomes high and workability gets remarkably bad, so that the molecular weight is generally large.

[0005] When the molecular weight of such a polymer is small, although viscosity becomes low, a hardened material is inferior to pliability. In order to make a polymer into hypoviscosity, maintaining the pliability of a hardened material until now, various kinds of plasticizers have been used.

[0006] As such a plasticizer, aromatic carboxylic acid ester, aliphatic-carboxylic-acid ester species, glycol ester, phosphoric ester, an epoxy plasticizer, a chlorinated paraffin, etc. are used. However, since these plasticizers are translatable, when it is used for a sealing material etc., there is a fault which has the surface contamination after contamination and paint of the ceiling part circumference and an adverse effect to an adhesive property.

[0007] The hardenability constituent which did not reduce the pliability of the hardened material and added the very low reactant plasticizer of translatibility was proposed by JP.5-59267.A to the polymer of the hygroscopic-surface-moisture hardenability which has a hydrolytic silicon group in order to cancel such a fault. However, in the use to a sealing material etc., when pliability is higher, it has the good characteristic of elongation and it paints on the surface, the hardenability constituent in which surface stain resistance has been improved is called for. Although various kinds of inorganic bulking agents are usually used in combination called a actual sealing material and adhesives, a polymer's own pliability is much more required for use of a bulking agent in order to harden the physical properties of a hardened material.

[0008] A terminal unsaturated group content polyether compound with molecular weight distribution narrow to JP.1-279958.A is mixed from such a viewpoint to a hydrolytic silicon group content polyether polymer, and the constituent which does not contain plasticizers, such as dioctyl phthalate, is indicated. However, when the addition of the terminal unsaturated group content polyether compound increased, the polyether which does not have a crosslinking group at all cozed out on the surface gradually after hardening, and especially the hardened material of such a constituent had a fault the hardened material surface comes to be alike of a fault all over.

[0009] Although the constituent which blends the narrow hydrolytic silicon group content polyether polymer of molecular weight distribution without a plasticizer was indicated to JP.5-65403.A, even if

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it did not use a plasticizer, it had practical viscosity, and when a hardened material was flexible, it had a fault to which hardening becomes very slow.

[0010] The example which furthermore mixes and uses two or more sorts of hydrolytic silicon group content polyether polymers in which the number of branching differs for JP.5-65405.A to JP.5-65406.A. The example which mixes and uses two or more sorts of hydrolytic silicon group content polyether polymers in which molecular weight distribution differs is shown. However, since there are more rates of the hydrolytic silicon group in all the molecular terminal groups of the polyether polymer which all mix than 80%, when especially inorganic bulking agents, such as calcium carbonate, are used, there is a fault applied to the pliability of a hardened material without a plasticizer.

[0011]

[Problem(s) to be Solved by the Invention] Then, even if the viscosity of the constituent could be satisfied practically and used the inorganic bulking agent, the hardened material was flexible, the extension characteristic of the hardened material was good, and as a result of examining the constituent which does not pollute a surface coat, it resulted in this invention.

[0012]

[Means for Solving the Problem] That is, this invention is the following invention. As opposed to polymer (I) [of the molecular weights 8000-30000], and polymer (II) 100 weight section whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups, A room-temperature-curing nature constituent in which less than 50% of all the molecular terminal groups contain one to polymer (III) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups, And a manufacturing method of a room-temperature-curing nature constituent characterized by mixing one to polymer (II) 200 weight section to polymer (I) 100 weight section.

[0013]

[Embodiment of the Invention] As for both polymer (I)s and polymer (II)s that are used by this invention, consisting of polyether intrinsically is [the main chain of a molecule] preferred. [0014] As for such a polymer, what is obtained by introducing a hydrolytic silicon group by the suitable method for a polyether containing hydroxyl group is preferred.

[0015] Such a polymer is proposed by JP.3-47825.A, JP.3-72527.A, JP.3-79627.A, JP.46-30711.B, JP.45-36319.B, JP.46-17553.B, etc., for example.

[0016] A polyether containing hydroxyl group is obtained by polymerizing monoepoxide, such as bottom alkylene oxide of existence of an initiator and a catalyst

[0017] The compound which has 2-10 active hydrogen as an initiator is preferred. A polyhydroxy compound is preferred and the polyhydroxy compound which has 2-4 hydroxyl groups especially is preferred 2-8 pieces. Specifically Ethylene glycol, a diethylene glycol, propylene glycol, Dipropylene glycol, neopentyl glycol, 1,4-butanediol, There is polyol of low molecular weight from the object produced by making monoepoxide react to 1,6-hexanediol, glycerin, trimethylolpropane,

pentaerythritol, diglycerol, a shock sirloin, and these. One-sort single use or two or more sorts of concomitant use may be sufficient as these. An unsaturation group content mono- hydroxy compound like allyl alcohol can also be used.

[0018] As monoepoxide, there are propylene oxide, butylene oxide, ethylene oxide, allyl glycidyl ether, etc. Especially propylene oxide is preferred. As a catalyst, catalysts, such as an alkaline metal catalyst, a composite metal cyanide complex catalyst, and metalloporphyrin, are mentioned.

[0019] Especially desirable polyethers containing hydroxyl group are polyoxypropylene diol, polyoxypropylene triol, polyoxypropylene tetraol, and polyoxypropylene hexaol. When using for following (1) or the method of (4), polyether of olefin ends, such as polyoxypropylene glycol monoallyl ether, can also be used.

[0020] The hydrolytic silicon group should just be a silicon group with which hydrolysis and crosslinking reaction occur with hygroscopic surface moisture. The silicon content group which has the hydrolytic basis coupled directly with the silicon atom can be used. For example, the basis expressed with a formula (A) is preferred.

[0021] $-R^2-SiR^1_3 \cdots (A)$

[0022] R^1 is a univalent organo group the substitution of the carbon numbers 1-20, or unsubstituted among a formula, R^2 is a divalent organic group, X is a hydroxyl group or a hydrolytic basis, and a is an integer of 1-3.

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[0023]As R¹ in a formula (A), a with a carbon number of eight or less alkyl group, a phenyl group, and a fluoro alkyl group are preferred, and a methyl group, an ethyl group, a propyl group, a butyl group, a hexyl group, a cyclohexyl group, especially a phenyl group, etc. are preferred.

[0024]X is a hydroxyl group or a hydrolytic basis, and there are a halogen atom, an alkoxy group, an acyloxy group, an amide group, an amino group, an aminooxy group, a KETOKISHI mate group, and a hydride group as a hydrolytic basis, for example. As for especially the carbon number of the hydrolytic basis which has a carbon atom among these, four or less are [six or less] preferred. As desirable X, a with a carbon number of four or less lower alkoxy group especially a methoxy group, an ethoxy basis, a propoxy group, etc. can be illustrated. As for a, 2 or 3 is preferred.

[0025]Next, the manufacturing method of polymer (I) and (II) is explained. These polymers introduce a hydrolytic silicon group into the end of a polyether containing hydroxyl group by a method like following the (1) - (4), and are manufactured.

[0026](1) A method to which the silicon hydride compound expressed with what introduced the unsaturation group into the end of hydroxyl group end polyether, and a formula (B) is made to react under existence of a catalyst.

[0027]HSiX_aR¹_{3-a} ... (B)

[0028]However, R¹ in formula X, and a are the same as the above.

[0029]Here, an unsaturation group is introduced or more into one of the end of hydroxyl group end polyether with what introduced the unsaturation group into the end of hydroxyl group end polyether.

After setting terminal hydroxyl groups OH of hydroxyl group end polyether to OM (M is an alkaline metal) as this method, There is the method of making the compound which has a functional group which can react to the method or unsaturation group, and hydroxyl group which are made to react to unsaturation group content halogenated hydrocarbon, such as an allyl chloride, react to hydroxyl group end polyether, and combining by the ester bond, a urethane bond, carbonate combination, etc. [0030]When polymerizing monoepoxide in manufacture of hydroxyl group end polyether, It is obtained also by using a terminal unsaturated group content mono- hydroxy compound as the method of introducing an unsaturation group into a side chain, or an initiator by carrying out copolymerization of the unsaturation group content monoepoxide, such as allyl glycidyl ether.

[0031](2) How to make the compound which has a hydrolytic silicon group expressed with an isocyanate group and a formula (A) react to hydroxyl group end polyether.

[0032](3) A method to which W basis of the silicon compound expressed with a formula (C) to this isocyanate group is made to react after making polyisocyanate compounds, such as tolylene diisocyanate, react to hydroxyl group end polyether and considering it as an isocyanate group end.

[0033]R¹_{3-a}-SiX_a-R^{3W} ... (C)

[0034]However, R¹ in formula X, and a are the same as the above, R³ is a divalent organic group, and W is the active hydrogen containing group chosen from the hydroxyl group, the carboxyl group, the sulfinyl group, and the amino group (the 1st class or the 2nd class).

[0035](4) A method to which the unsaturation group of the thing which introduced the unsaturation group into the end of hydroxyl group end polyether, and the sulfinyl group of a silicon compound expressed by the formula (C) whose W is a sulfinyl group are made to react.

[0036]The hydrolytic silicon cardinal numbers of polymer (I) of this invention are not less than 50% of 100% or less of all the molecular terminal groups, and are desirable. [not less than 60% of 100% or less of] As for the molecular terminal cardinal number per molecule, 2-8 are preferred, and 2- especially 4 are preferred.

[0037]The hydrolytic silicon groups of polymer (II) of this invention are less than 50% of all the molecular terminal groups, and are desirable. [not less than 25% of less than 50% of] As for the molecular terminal cardinal number per molecule, 2-8 are preferred, 3- especially 8 are preferred, and 3-6 are still more preferred.

[0038]As polymer (I) of this invention, the polymer of the molecular weights 8000-30000 can be used. Especially when the molecular weight of this polymer is lower than 8000, in order to make a hardened material flexible, the rate of the hydrolytic silicon group of all the molecular terminal groups must be lessened as compared with what has a bigger molecular weight, and the fault that hardenability worsens arises. When a molecular weight exceeds 30000, also after mixing with polymer (II), workability gets remarkably bad for hyperviscosity. Desirable molecular weights are 10000-20000.

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[0039]As polymer (II) of this invention, the polymer of the molecular weights 4000-30000 can be used. Even if it mixes with polymer (I), especially when hardenability will become bad when the molecular weight of this polymer is lower than 4000 and a molecular weight exceeds 30000, workability gets remarkably bad for hyperviscosity. Desirable molecular weights are 8000-20000.

[0040]The molecular weight of polymer (I) and polymer (II) is computed based on the hydroxyl value conversion value molecular weight of hydroxyl group end polyether which is a raw material.

[0041]In this invention, 1-200 weight-section use of polymer (II) is carried out to polymer (I) 100 weight section. 20-100 weight-section use of polymer (I) is carried out especially preferably ten to 150 weight section.

[0042]The room-temperature-curing nature constituent in this invention can be manufactured by mixing one to polymer (II) 200 weight section to polymer (I) 100 weight section.

[0043]Thus, the advantage of mixing and using two or more sorts of polymers is that the physical properties of the hardened material produced by making harden a hardenability constituent with the ratio to mix are controllable. If this method is used, by the variety of few polymers, many hardened material physical properties will be made to reveal quite freely, and it will get. That is, a more flexible hardened material is obtained by a hard hardened material being obtained by increasing the amount of polymer (I) used, and increasing the amount of polymer (II) used, and the middle can be chosen arbitrarily.

[0044]In the constituent of this invention, if necessary to publicly known various curing catalysts, a bulking agent, an additive agent, and a pan, a solvent, a plasticizer, etc. can be included.

[0045]The following compound can be used as a curing catalyst. Metal salt, such as an alkyl titanate, an organic silicon titanate, and bismuth tris-2-ethylhexoate. Acidic compounds, such as phosphoric acid, p-toluenesulfonic acid, and phthalic acid, a butylamine. Aliphatic series monoamines, such as hexylamine, octylamine, decyl amine, and lauryl amine. Aliphatic diamine, such as ethylenediamine and a hexanediamine, diethylenetriamine, Aliphatic polyamine, such as triethylenetetramine and tetraethylenepentamine. Amine compounds, such as aromatic amine, such as heterocyclic amine, such as piperidine and a piperazine, and a meta-phenylenediamine, ethanalamines, triethylamine, and various denaturation amine used as a hardening agent of an epoxy resin.

[0046]Divalent tin and the mixture of the above-mentioned amines of tin dioctylate, JINAFUTEN

***, distearic acid tin, etc.

[0047]Dibutyltin dilaurate, dibutyltin dilaurate, dioctyl tin dilaurate, the following carboxylic type organic tin compound, and the mixture of these carboxylic type organic tin compounds and the above-mentioned amines. (n-C₄H₉)₂Sn(OCOCH=CHCOOCH₃)₂, (n-C₄H₉)₂Sn

(OCOCH=CHCOOCH₃H_{9-n})₂, (n-C₈H₁₇)₂Sn(OCOCH=CHCOOCH₃)₂, (n-C₈H₁₇)₂Sn

(OCOCH=CHCOOCH₃H_{9-n})₂, (n-C₈H₁₇)₂Sn(OCOCH=CHCOOCH₃H_{17-n})₂

[0048]The following sulfur-containing mold organic tin compound. (n-C₄H₉)₂Sn(SCH₂COO), (n-

C₈H₁₇)₂Sn(SCH₂COO), (n-C₈H₁₇)₂Sn(SCH₂CH₂COO), (n-C₈H₁₇)₂Sn

(SCH₂COOCH₂CH₂COOCH₃S), (n-C₄H₉)₂Sn(SCH₂COOCH₃H_{17-iso})₂, (n-C₈H₁₇)₂Sn

(SCH₂COOCH₃H_{17-iso})₂, (n-C₈H₁₇)₂Sn(SCH₂COOCH₃H_{17-n})₂, and (n-C₄H₉)₂SnS.

[0049](n-C₄H₉) Organic tin oxide, such as SnO and (n-C₈H₁₇)₂SnO. And the resultant of these

organic tin oxide and ester compounds, such as ethyl silicate, dimethyl maleate, a diethyl maleate, dioctyl maleate, dimethyl phthalate, diethyl phthalate, and dioctyl phthalate.

[0050]Chelate tin compounds, such as the following, and the resultant of these tin compounds and alkoxy silanes (however, acac acetylacetonate ligand). (n-C₄H₉)₂Sn(acac)₂, (n-C₈H₁₇)₂Sn(acac)₂, and

(n-C₄H₉)₂(C₈H₁₇-O)Sn(acac).

[0051]The following tin compound. (n-C₄H₉)₂(CH₃COO)SnOSn(OCOCH₃)₂(n-C₄H₉)₂(n-C₄H₉)₂

(CH₃O)SnOSn(OCH₃)₂(n-C₄H₉)₂

[0052]If it is considered as a bulking agent, the publicly known following bulking agent can be used. The calcium carbonate which carried out the surface treatment of the surface with fatty acid or a

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resin acid system organio matter, Colloid calcium carbonate with a mean particle diameter of 1 micrometer or less which furthermore impalpable—powder—ized this, Calcium carbonate, such as precipitated calcium carbonate with a mean particle diameter of 1-3 micrometers manufactured with the sedimentation method, and heavy calcium carbonate with a mean particle diameter of 1-20 micrometers, Fumes silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, and carbon black, Magnesium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, a milt balloon, wood flour, pulp, a cotton chip, mica, and the blacking wash farina — rubbing — powder state bulking agents, such as farina, graphite, aluminum impalpable powder, and the Flint powder. Fibrous fillers, such as asbestos, glass fiber, a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber.

[0053]As for especially the amount of the bulking agent used, 50 to 250 % of the weight is preferred one to 1000% of the weight to the sum total of polymer (I) and polymer (II). These bulking agents may be used independently and may be used together two or more sorts.

[0054]A plasticizer may be used, although the room-temperature-curing nature constituent in this invention is fully hypoviscosity in itself and it is preferred not to use a plasticizer substantially. As a plasticizer, for example Dioctyl phthalate, dibutyl phthalate, Phthalic acid alkyl ester, such as phthalic acid benzyl butyl ester, Dioctyl adipate, Glucol ester species, such as aliphatic-carboxylic-acid alkyl ester; pentaerythritol ester, such as succinic acid diisodecyl, dibutyl sebacate, and butyl oleate; Triocetyl phosphate, Phosphoric ester, such as tricresyl phosphate; epoxy plasticizer; chlorinated paraffin, such as epoxidized soybean oil and epoxy stearic acid benzyl, etc. can be independent, or can use it with two or more sorts of mixtures.

[0055]However, a low molecule plasticizer has the problem which is this invention of being easy to carry out after [room-temperature-curing nature constituent hardening] bleed out, among such plasticizers, and it is preferred not to use it. That is, it is preferred for the room-temperature-curing nature constituent of this invention to contain a plasticizer further, and not to contain a low molecule plasticizer as the plasticizer. The compound itself is low molecular weight, and a low molecule plasticizer refers to the plasticizer which does not have a reactant group. For example, it is phthalic acid alkyl ester.

[0056]To the constituent of this invention, a hydrolytic silicon compound can be arbitrarily added in order to adjust physical properties and hardenability of a hardened material. As such a compound, specifically Tetramethyl silicate, vinyltrimethoxysilane, Although the compound etc. in which methyl trimethoxysilane, dimethyldimethoxysilane, trimethylmethoxysilane, etc. and these methoxy groups were replaced by the ethoxy basis can be illustrated, it is not limited to these.

[0057]As an additive agent, the photoresist compound aiming at adhesion grant agents, such as a thioxotropy grant agent, phenol resin, an epoxy resin, etc. and various kinds of silane coupling agents, paints, various kinds of stabilizer, and surface treatment like oligoester acrylate etc. are mentioned. A solvent can also be used in order to prepare viscosity.

[0058]The room-temperature-curing nature constituent of this invention can be used as a sealing material especially an elastic sealing compound, and adhesives.

[0059] [Example]Although a synthetic example, working example, and a comparative example are given to below and this invention is explained to it still in detail, this invention is not limited to these. As for the synthetic examples 1-6, the synthetic example 13 of polymer (II) of the synthetic examples 7-12 of polymer (I) is a synthetic example of the polymer for comparison.

[0060][Synthetic example 1] Ethylene glycol was used as the initiator, and it refined, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene diol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. The polymer a of the molecular weight 17000 [about] which made it react to methyl dimethoxysilane by having made chloroplatinic acid into the catalyst furthermore, and introduced the methyl dimethoxy silyl propyl group into 60% of all the molecular terminal groups was compounded. The viscosity in 25 ** was 15000cP.

[0061][Synthetic example 2] The polymer b of the molecular weight 17000 [about] which introduced the methyl dimethoxy silyl propyl group into 75% of all the molecular terminal groups by the same method as the synthetic example 1 was compounded. The viscosity in 25 ** was 15200cP.

[0062][Synthetic example 3] Glycerin was used as the initiator, and it refined, after changing into an

allyloxy group the terminal hydroxyl groups of the polyoxypropylene triol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. The polymer c of the molecular weight 18000 [about] which made it react to methyl dimethoxysilane by having made chloroplatinic acid into the catalyst furthermore, and introduced the methyl dimethoxy silyl propyl group into 60% of all the molecular terminal groups was compounded. The viscosity in 25 ** was 10500cP.

[0063][Synthetic example 4] The polymer d of the molecular weight 10000 [about] which introduced the methyl dimethoxy silyl propyl group into 84% of all the molecular terminal groups by the same method as the synthetic example 3 was compounded. The viscosity in 25 ** was 3000cP.

[0064][Synthetic example 5] The polymer e of the molecular weight 15000 [about] which introduced the methyl dimethoxy silyl propyl group into 91% of all the molecular terminal groups by the same method as the synthetic example 3 was compounded. The viscosity in 25 ** was 8800cP.

[0065][Synthetic example 6] Ethylene glycol was used as the initiator, and it refined, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene diol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. After making methyl dimethoxysilane of a 120% considerable amount react to all the molecular terminal groups by making chloroplatinic acid into a catalyst furthermore, the unreacted material was distilled off under decompression, and the polymer f of the molecular weight 9000 [about] which introduced the methyl dimethoxy silyl propyl group into the end was compounded. The viscosity in 25 ** was 5400cP.

[0066][Synthetic example 7] The polymer g of the molecular weight 18000 [about] which introduced the methyl dimethoxy silyl propyl group into 35% of all the molecular terminal groups by the same method as the synthetic example 3 was compounded. The viscosity in 25 ** was 10500cP.

[0067][Synthetic example 8] The polymer h of the molecular weight 9000 [about] which introduced the methyl dimethoxy silyl propyl group into 35% of all the molecular terminal groups by the same method as the synthetic example 3 was compounded. The viscosity in 25 ** was 2800cP.

[0068][Synthetic example 9] Glycerin was used as the initiator, and it refined, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene triol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. The polymer i of the molecular weight 9000 [about] which made it react to methyl dimethoxysilane by having made chloroplatinic acid into the catalyst furthermore, and introduced the methyl dimethoxy silyl propyl group into 45% of all the molecular terminal groups was compounded. The viscosity in 25 ** was 2800cP.

[0069][Synthetic example 10] Pentaerythritol was used as the initiator, and it refined, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene tetraol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. The polymer j of the molecular weight 17000 [about] which made methyl dimethoxysilane react by having made chloroplatinic acid into the catalyst furthermore, and introduced the methyl dimethoxy silyl propyl group into 35% of all the molecular terminal groups was compounded. The viscosity in 25 ** was 6000cP.

[0070][Synthetic example 11] The polymer k of the molecular weight 8000 [about] which introduced the methyl dimethoxy silyl propyl group into 25% of all the molecular terminal groups by the same method as the synthetic example 10 was compounded. The viscosity in 25 ** was 2000cP.

[0071][Synthetic example 12] Sorbitol was used as the initiator, and it refined, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene hexaol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react. Methyl dimethoxysilane was made to react by having made chloroplatinic acid into the catalyst furthermore, and the polymer l of the molecular weight 12000 [about] which introduced the methyl dimethoxy silyl propyl group into 20% of all the molecular terminal groups was compounded. The viscosity in 25 ** was 2200cP.

[0072][Synthetic example 13] Glycerin was used as the initiator, after changing into an allyloxy group the terminal hydroxyl groups of the polyoxypropylene triol produced by making the bottom propylene oxide of existence of a zinc hexa cyanocobaltate complex compound catalyst react, it refined, and the polymer m of the molecular weight 9000 [about] was obtained. The viscosity in 25 ** was 2500cP.

[0073][Working example 1-6 and comparative examples 1-6] It mixed at a rate given [polymer (I), polymer (II) (or polymer for comparison) or them, and dioctyl phthalate (DOP)] in Tables 1-2, mixed liquor was obtained, and the viscosity (unit: cP) at the 25 °C was measured.

[0074][Next, mixed liquor 160 weight section (it is hereafter considered as a part) of a polymer (or a polymer and DOP) is received, 75 copies of calcium carbonate (Shiroishi calcium company make, Hakenka CGR), and calcium carbonate (Shiroishi calcium company make.) 75 copies of HOWAITON SB, 30 copies of titanium dioxides, and stabilizer (an antioxidant.) The mixture of an ultraviolet ray absorbent and light stabilizer, the Ciba-Geigy make, tinuvin B752 copy, Five copies of photo-setting resins (the Toagosei Chemical Industry Co., Ltd. make, ARONIKUSU M6020), two copies of silane coupling agents (the Shin-Etsu Chemical Co., Ltd. make, KBM603), and DISUPARON 6500 (made in Kusumoto Chemicals.) It kneaded under the conditions which add fatty-acid-amide system thixotropy grant agent 1 copy and two copies of dibutyl tin bisacetylacetonate (the Nihon Kagaku Sangyo Co., Ltd. make, NASEMUSUZU), and moisture does not mix, and was considered as the uniform mixture. Subsequently, the following (1) - (5) was evaluated and the result was shown in Tables 1-2.

[0075](1) 50% modulus (unit: kg/cm²), breaking strength (unit: kg/cm²), and after being extended (unit: %) and using mixture as a sheet about 2 mm thick. After carrying out cure for seven days at 50 °C subsequently for seven days at 20 °C, it measured about what was pierced with the JIS No. 3 dumbbell.

[0076](2) Hardenability : the hardenability after 6-hour neglect was judged for the mixture by finger touch under the condition of 20 °C and 65%RH. It was assumed that that from which O is a tuck freelaner in evaluation, and x are not a tuck freelaner.

[0077](3) Pliability of a hardened material : the pliability of the hardened material in which carried out cure of this mixture and it was obtained was also evaluated. O or [that x which has pliability desirable as a sealing material for construction is too hard as a sealing material for construction] -- or it was presupposed that it is too soft.

[0078](4) Aging : there is no bleed out, such as an unreacted material, in the surface after two-week neglect at 50 °C, or the unpainted hardened material surface was examined by finger touch. O As for what bleed out was not accepted to, and x, bleed out should be accepted.

[0079](5) Stain resistance of a paint surface : after painting a solvent system alkyd paint (the Rock Paint Co., Ltd. make, house paint) to what was stiffened as a 1-cm thickness sheet, and one month after being exposed to the outdoors after one-week heating at 70 °C, the dirt situation of the paint surface was observed. O Although dirt had adhered a little, a beautiful thing and x assumed that adhesion of dust etc. is remarkable and dirty.

[0080]In the case (the comparative example 2, the comparative example 4) where polymer (II) is not used, the pliability in which a hardened material is too hard and it is desirable as a sealing material cannot be revealed as a table shows. A paint film surface is made to pollute with the compound which uses dioctyl phthalate, and it is not desirable what performed surface coating. In the case where the polymer in which one does not have a hydrolytic silicon group is used, the polymer for which a bridge is not constructed over the hardened material surface carries out bleed out from a hardened material, and it is not desirable.

[0081]

[Table 1]

実施例	1	2	3	4	5	6
a	70	70	70	70	100	100
b	30	30	30	30		
c	60	60	60	60		
d						
e						
f						
g						
h						
i						
j						
k						
l						
粘度	12500	9600	9600	10800	7000	10300
50%モジュラス	1.0	1.1	1.3	0.9	1.9	1.7
破断強度	5.8	6.0	6.4	5.6	7.9	8.2
伸び	830	810	790	820	750	650
硬化性	○	○	○	○	○	○
硬化物の柔軟性	○	○	○	○	○	○
経時変化	○	○	○	○	○	○
塗装表面の汚染性	○	○	○	○	○	○

[0082]

[Table 2]

比較例	1	2	3	4	5	6
a	70		70	112		80
c	30		30	48		80
d		160				
e						
f						
g					160	
m	60					
DOP			60			
粘度	9500	3000	8200	13700	10500	7100
50%モジュラス	0.8	4.2	2.0	3.0	0.4	4.0
破断強度	5.8	9.5	8.0	8.5	2.5	9.0
伸び	820	480	750	720	950	520
硬化性	○	○	○	○	×	○
硬化物の柔軟性	○	×	○	×	×	×
経時変化	×	○	○	○	○	○
塗装表面の汚染性	○	○	×	○	○	○

[0083]

[Effect of the Invention] Even if the room-temperature-curing nature constituent of this invention has low viscosity enough and it uses an inorganic bulking agent, it has the effect of not reducing the pliability of a hardened material. When the constituent of this invention is used for a sealing material etc., it does not have contamination or the adverse effect to an adhesive property of the ceiling part circumference or a paint surface.

[Translation done.]

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.*** shows the word which can not be translated
3. In the drawings, any words are not translated.

CORRECTION OR AMENDMENT

[Kind of official gazette] Printing of amendment by regulation of Patent Law Article 17 of 2

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[Amendment 1]

[Document to be Amended] Description

[Item(s) to be Amended] Claims

[Method of Amendment] Change

[Proposed Amendment]

[Claim(s)]

[Claim 1] Polymer (I) of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups, And a room-temperature-curing nature constituent in which less than 50% of all the molecular terminal groups contain one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups to polymer (I) 100 weight section.

[Claim 2] The room-temperature-curing nature constituent according to claim 1 whose both main chain of polymer (I) and main chain of polymer (II) are polyether intrinsically.

[Claim 3] The room-temperature-curing nature constituent according to claim 1 or 2 in which a room-temperature-curing nature constituent does not contain a plasticizer substantially.

[Claim 4] The room-temperature-curing nature constituent according to claim 1 or 2 which a room-temperature-curing nature constituent contains a plasticizer further, and does not contain a low molecule plasticizer as the plasticizer.

[Claim 5] As opposed to polymer (I) 100 weight section of the molecular weights 8000-30000 whose not less than 50% of all the molecular terminal groups are hydrolytic silicon groups, A manufacturing

method of a room-temperature-curing nature constituent, wherein less than 50% of all the molecular terminal groups mix one to polymer (II) 200 weight section of the molecular weights 4000-30000 which are hydrolytic silicon groups.

[Amendment 2]

[Document to be Amended] Description

[Item(s) to be Amended] 0003

[Method of Amendment] Change

[Proposed Amendment]

[0003] The polymer especially whose main chain is polyether among such compounds is liquefied at a room temperature, and when a hardened material holds pliability also at low temperature comparatively and uses for a sealing material, adhesives, etc., it is provided with the desirable characteristic.

[Amendment 3]

[Document to be Amended] Description

[Item(s) to be Amended] 0007

[Method of Amendment] Change

[Proposed Amendment]

[0007] The hardenability constituent in which the pliability of the hardened material was not reduced and translatability added the very low reactant plastioizer was proposed by JP.5-59267.A to the polymer of the hygroscopic-surface moisture hardenability which has a hydrolytic silicon group in order to cancel such a fault. However, in the use to a sealing material etc., when pliability is higher, it has the good characteristic of elongation and it paints on the surface, the hardenability constituent in which surface stain resistance has been improved is called for. Although various kinds of inorganic bulking agents are usually used in combination called a actual sealing material and adhesives, a polymer's own pliability is much more required for use of a bulking agent in order to harden the physical properties of a hardened material.

[Amendment 4]

[Document to be Amended] Description

[Item(s) to be Amended] 0038

[Method of Amendment] Change

[Proposed Amendment]

[0038] As polymer (I) of this invention, the polymer of the molecular weights 8000-30000 can be used. Especially when the molecular weight of this polymer is lower than 8000, in order to make a hardened material flexible, the fault which must lessen the rate of the hydrolytic silicon group of all the molecular terminal groups as compared with what has a bigger molecular weight and to which hardenability worsens arises. When a molecular weight exceeds 30000, also after mixing with polymer (II), workability gets remarkably bad for hyperviscosity. Desirable molecular weights are 10000-20000.

[Amendment 5]

[Document to be Amended] Description

[Item(s) to be Amended] 0039

[Method of Amendment] Change

[Proposed Amendment]

[0039] As polymer (II) of this invention, the polymer of the molecular weights 4000-30000 can be used. Especially when the molecular weight of this polymer is lower than 4000, even if it mixes with polymer (I), hardenability will become bad, and when a molecular weight exceeds 30000, workability gets remarkably bad for hyperviscosity. Desirable molecular weights are 8000-20000.

[Amendment 6]

[Document to be Amended] Description

[Item(s) to be Amended] 0045

[Method of Amendment] Change

[Proposed Amendment]

[0045] The following compound can be used as a curing catalyst. Metal salt, such as an alkyl titanate, an organic silicon titanate, and bismuth tris-2-ethylhexanoate. Acidic compounds, such as phosphoric acid, p-toluenesulfonic acid, and phthalic acid, a butylamine. Aliphatic series monoamines, such as hexylamine, octylamine, decyl amine, and lauryl amine. Aliphatic diamine, such as ethylenediamine and a hexanediamine, diethylenetriamine, Aliphatic polyamine, such as triethylenetetramine and

tetraethylenepentamine. Amine compounds, such as aromatic amine, such as heterocyclic amine, such as piperidine and a piperazine, and a meta-phenylenediamine, ethanalamines, triethylamine, and various denaturation amine used as a hardening agent of an epoxy resin.

[Amendment 7]

[Document to be Amended]Description

[Item(s) to be Amended]0052

[Method of Amendment]Change

[Proposed Amendment]

[0052]If it is considered as a bulking agent, the publicly known following bulking agent can be used. The calcium carbonate which carried out the surface treatment of the surface with fatty acid or a resin acid system organic matter, Colloid calcium carbonate with a mean particle diameter of 1 micrometer or less which furthermore impalpable-powder-ized this, Calcium carbonate, such as precipitated calcium carbonate with a mean particle diameter of 1-3 micrometers manufactured with the sedimentation method, and heavy calcium carbonate with a mean particle diameter of 1-20 micrometers, Fumed silica, sedimentation nature silica, a silicic acid anhydride, hydrous silicic acids, carbon black, Magnesium carbonate, diatomite, calcination clay, clay, talc, titanium oxide, Powder state bulking agents, such as bentonite, organic bentonite, ferric oxide, a zinc oxide, an active white, a mill balloon, wood flour, pulp, a cotton chip, mica, blacking wash shell flour, chaff powder, graphite, aluminum impalpable powder, and the Flint powder. Fibrous fillers, such as glass fiber, a glass filament, carbon fiber, the Kevlar textiles, and a polyethylene fiber.

[Amendment 8]

[Document to be Amended]Description

[Item(s) to be Amended]0054

[Method of Amendment]Change

[Proposed Amendment]

[0054]A plasticizer may be used, although the room-temperature-curing nature constituent in this invention is fully hypoviscosity in itself and it is preferred not to use a plasticizer substantially. As a plasticizer, for example Dioctyl phthalate, dibutyl phthalate, Phthalic acid alkyl ester, such as phthalic acid benzyl butyl ester, Dioctyl adipate, Aliphatic-carboxylic-acid alkyl ester, pentaerythritol ester, such as succinic acid diisodecyl, dibutyl sebacate, and butyl oleate etc.; Trioctyl phosphate, Phosphoric ester, such as triresyl phosphate; epoxy plasticizer; chlorinated paraffin; such as epoxidized soybean oil and epoxy stearic acid benzyl, etc. can be independent, or can use it with two or more sorts of mixtures.

[Amendment 9]

[Document to be Amended]Description

[Item(s) to be Amended]0055

[Method of Amendment]Change

[Proposed Amendment]

[0055]However, a low molecule plasticizer has a problem this invention tends to carry out [a problem] after [room-temperature-curing nature constituent hardening] bleed out among such plasticizers, and it is preferred not to use it. That is, it is preferred for the room-temperature-curing nature constituent of this invention to contain a plasticizer further, and not to contain a low molecule plasticizer as the plasticizer. The compound itself is low molecular weight, and a low molecule plasticizer refers to the plasticizer which does not have a reactant group. For example, it is phthalic acid alkyl ester.

[Amendment 10]

[Document to be Amended]Description

[Item(s) to be Amended]0083

[Method of Amendment]Change

[Proposed Amendment]

[0083]

[Effect of the Invention]Even if the room-temperature-curing nature constituent of this invention has low viscosity enough and it uses an inorganic bulking agent, it has the effect of not reducing the pliability of a hardened material. When the constituent of this invention is used for a sealing material etc., it does not have contamination or the adverse effect to an adhesive property of the ceiling part circumference or a paint surface.

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[Translation done.]

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